Transient behavior of Cu/ZnO-based methanol synthesis catalysts

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Introduction

Methanol is synthesized industrially by passing "syngas" (a mixture of H_2, CO and CO_2) over a $Cu/ZnO/Al_2O_3$-based catalyst [1]. It is known that (pre)treatment of such a methanol catalyst in a reducing H_2/CO mixture gives rise to a transient overproduction of methanol when the feed gas is changed back to synthesis gas (containing CO_2) [2,3]. One possible explanation for this activity transient is that during pretreatment in H_2/CO the Cu particles change to a flat, high surface area, morphology so that when CO_2 is introduced a high turnover occurs. However, since synthesis gas has a lower reduction potential than the pretreatment gas the Cu-particles revert to a less flat (and less active) morphology which causes decay in methanol turnover after the initial peak [2].
We have systematically mapped out how the methanol transient depends on the H_2/CO ratio in the pretreatment gas showing for the first time a clear synergy between H_2 and CO. To provide direct support for this synergy we have done an extensive study of a Cu/ZnO catalyst in an Environmental TEM (ETEM) under relevant gas mixtures. The ETEM data support the synergy between CO and H_2 in that Cu particles are more flat in H_2/CO mixtures than in either pure H_2 or pure CO.

Materials and Methods

Methanol synthesis measurements to map out the how the Methanol transient depends on pretreatment conditions were carried out over 1g of crushed $Cu/ZnO/Al_2O_3$ catalyst in a quartz tube plug flow reactor with quadrupole mass-spectrometry detection of products. These experiments were carried out at a total pressure of 4 bar and at 500 K.

ETEM experiments were carried out using a Cu/ZnO model catalyst under many gas mixtures including pure H_2, pure CO, H_2/CO mixtures, synthesis gas and wet synthesis gas. The total pressure in the ETEM was maintained at 2 mbar and the temperature was 500 K. The ETEM instrument was a Philips CM300 ST FEG-TEM equipped with differential pumping apertures [4]. The morphology of the Cu particles was extracted from the ETEM images using a new "Wulff-circle" method which allows the use of pictures without lattice resolution. This greatly enhances the number of useful images giving better statistics.

Results and Discussion

The methanol synthesis experiments using the H_2/CO ratio of the pretreatment gas as parameter reveal a very strong synergy between H_2 and CO: Pretreatment in pure H_2 gives no transient methanol peak (fig. A), but intermediate mixtures of H_2 and CO give a large peak. Pure CO gives no methanol peak. Figure B shows the ETEM-derived average Cu-particle shape data. From this it is clearly seen that the lowest b/a-value (most flat morphology) is associated with the 1:1 H_2:CO mixture - *not* with pure CO or H_2! Furthermore we see that the addition of steam to the feed gas (wet gasses) also has a pronounced effect causing the particles to become more spherical (less flat). Steam is known to dramatically reduce methanol synthesis rates under industrial conditions which again indicates the relationship between shape (b/a) and activity. This observation has previously been used to establish a microkinetic model for methanol synthesis over $Cu/ZnO/Al_2O_3$ catalysts [5]. We relate our findings to this model and from ETEM data we try to estimate ΔG for the surface reduction of the ZnO support.

Significance

The newly discovered synergy between H_2 and CO in pre-reduction of $Cu/ZnO(/Al_2O_3)$ catalysts expands our understanding of the complex $Cu/ZnO/Al_2O_3$ system - particularly to the gas-shape-activity relationship. It also raises new questions about the physics behind the synergy which future work should explore.

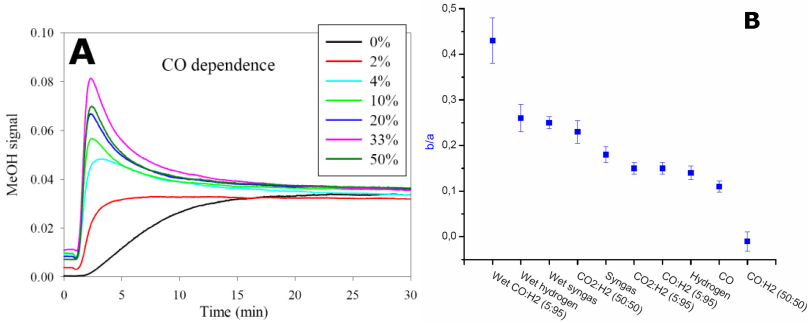

Figure A. Plot of methanol synthesis transient. The legend shows the pretreatment gas composition and the change to synthesis gas is made at t=0.
Figure B. Cu particle shape derived from ETEM images (given by the dimensionless parameter "b/a". Sphere: b/a=1, hemisphere: b/a=0, flat layer: b/a=-1) as a function of gas composition.

References

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